

Thermally Stable Ultra-Low Temperature Oxidation Catalysts

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This presentation does not contain any proprietary, confidential, or otherwise restricted information.

ACE027

June 19, 2014

Timeline

- Start – October 2013
- Finish – September 2016
- 17% Complete

Budget

- Total project funding
 - DOE – \$750K
 - GM – \$450K

Barriers

- Discussed on next slide

Partners

- Pacific Northwest National Laboratory
- General Motors Global R&D





Future Automotive Aftertreatment Solutions: The 150°C Challenge Workshop Report

ACEC Low Temperature Aftertreatment Group

*Michael Zammit and Craig DiMaggio(Chrysler), Chang Kim(GM), Christine Lambert(Ford),
George Muntean(PNNL), Chuck Peden(PNNL), Jim Parks(ORNL),
Ken Howden(DOE)*

- Low Temperature Activity: Catalysts do not currently achieve significant activity performance until ~200 °C. Performance at lower temperatures (>90% conversion at 150 °C) is desired. Added to address comment from Steve Overbury that we should spell out low temperature driver.
- Catalysts must be stable to meet durability requirements, and stabilization will enable lower temperature performance for light-off. Sintering of active metal sites is a major barrier.
- Low-T limits of current and developing aftertreatment technologies need to be accurately established including, for example, fundamental studies aimed at determination of reaction mechanisms and catalyst structure/function.



- In this GM-PNNL CRADA, PNNL will investigate a number of candidate **low temperature oxidation catalysts as fresh materials, and after realistic laboratory- and engine-aging.** Some specifics for the initial catalyst materials to be studied are contained in GM's recent patent disclosure on non-PGM based ultra low temperature oxidation catalysts.
- The studies being performed here are aimed at:
 - Better understanding of fundamental chemical and physical properties of the non-precious metal-based catalysts.
 - Determination of various aging factors that impact the long-term performance of new generation low temperature oxidation catalysts.
 - Assessment of the appropriateness of the laboratory conditions in realistically reproducing the effects of actual engine aging conditions.
- Figures of merit:
 - T_{50} for CO and hydrocarbon oxidation of ~ 150 °C.
 - Stable performance after 750 °C for 72 hr under 10% H₂O/air (~ 120 kilo miles).



- **Prepare and Process non-PGM low temperature CO and HC oxidation catalysts**
 - To date, all catalyst samples (fresh and high temperature aged) have been provided by GM in powder form. Reactor testing and aging being performed at GM.
 - PNNL will also synthesize some standard and novel catalysts based on developing structure/function relationships identified here.
- **Utilize catalysis expertise, and state-of-the-art catalyst characterization and testing facilities in PNNL's IIC to determine structure/activity relationships and deactivation mechanisms**
 - XRD, XPS, EPR, TEM/EDX and SEM/EDX
 - CO, NO TPD, FTIR
 - Lab reactor studies





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Sample Preparation

- Laboratory Aging

Measurement

- Initial Materials Characterization
- Catalytic Activity

Characterization

- *in-situ* XRD
- TEM/EDX
 - XPS
 - FTIR
 - EPR
- TPD/TPR

OCT-2013 → SEPT-2016

- *Jointly use new understandings to develop new and improved catalysts for low-temperature CO and hydrocarbon oxidation.*
- Kick-off meeting held at PNNL, November 1, 2013.
- Conference calls are held 5-7 times a year to discuss the results.
- Annual face-to-face meeting will be scheduled for later this year.

Results shown today are largely preliminary.

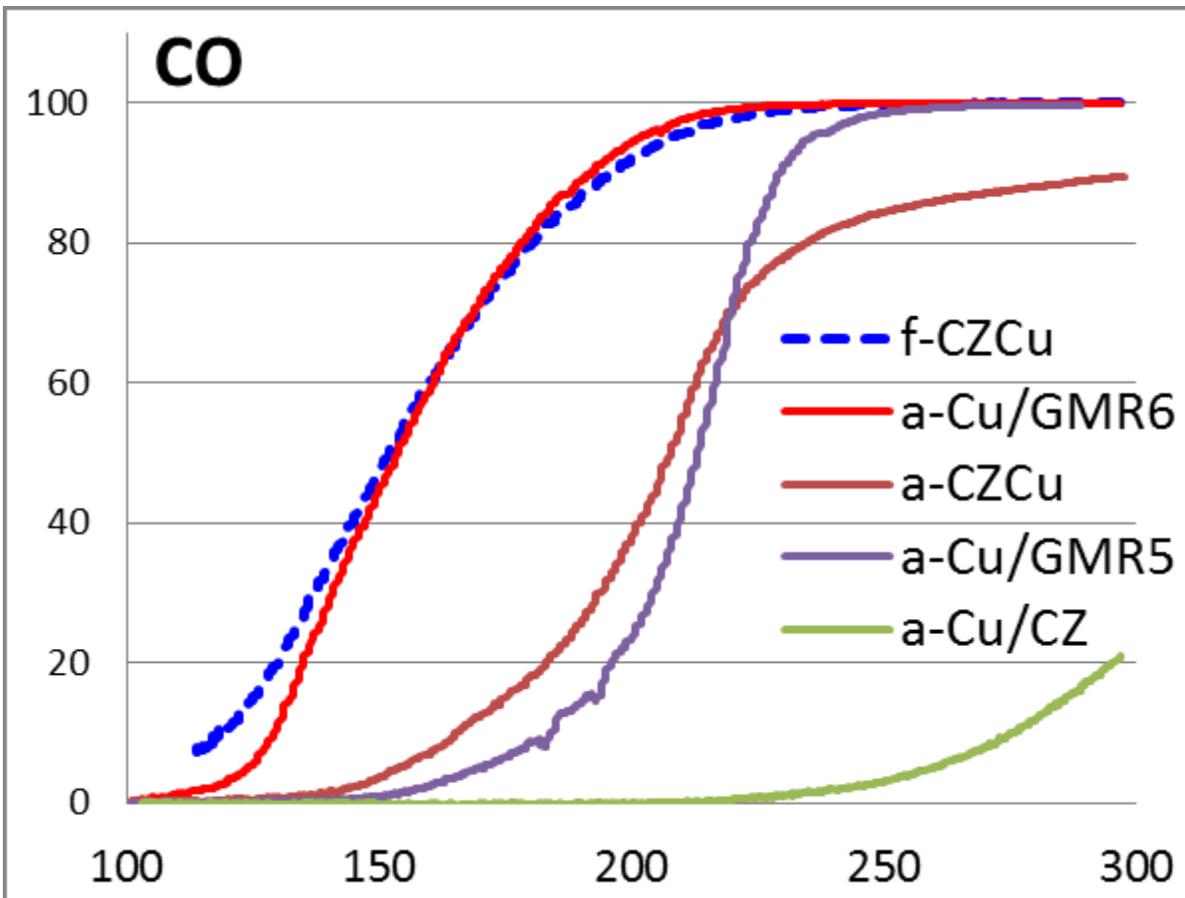


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Initial Promising Results

Feed: 500 ppm CO, 260 ppm C₃H₆, 87 ppm C₃H₈, 200 ppm NO, 8% O₂, 8% H₂O and N₂ bal.; Flow rate: 300 sccm, GHSV=170,000 h⁻¹; Temperature ramping: 2 °C/min



- Laboratory-prepared CZ-supported Cu catalyst (CZCu) strongly deactivate during hydrothermal aging.
- Commercial CZ-supported Cu catalyst (Cu/GMR6) after hydrothermal aging was as active as the fresh CZCu catalyst.
- **Some initial questions:**
 - What makes the commercial CZ much better support?
 - What is the nature of the active Cu species?
 - Reaction mechanism?

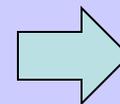
Chang H. Kim, Iljeong Heo, Se H. Oh, Wei Li, and Michelle H. Schmid, "Oxidation Catalysts for Engines Producing Low Temperature Exhaust Streams", Patent Application US 2012/0291420 A1 (11/22/2012).



Physical Properties of Fresh and Aged Catalysts

Physical Properties of Fresh and Aged Catalysts: BET surface area (m²/g)

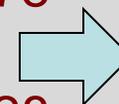
<u>Sample</u>	<u>Fresh</u>	<u>Aged</u>	<u>S_{final}/S_{initial}</u>
CZ	171	59	0.35
Cu/CZ	122	0.4	0.003
CZCu	123	6	0.05
GMR6	66	59	0.89
Cu/GMR6	53	30	0.57



BET surface area (SA) decrease upon hydro-thermal aging:
Cu/CZ SA loss is much greater than Cu/GMR6

Cu particle size by XRD (Deby-Sherrer's eqn.)

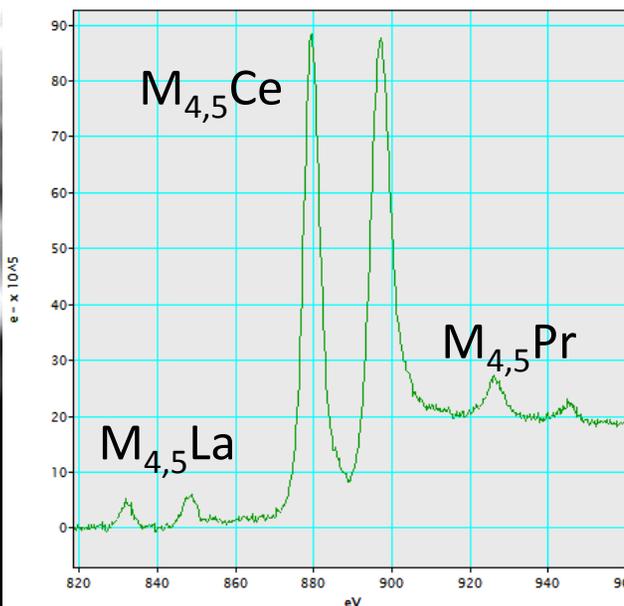
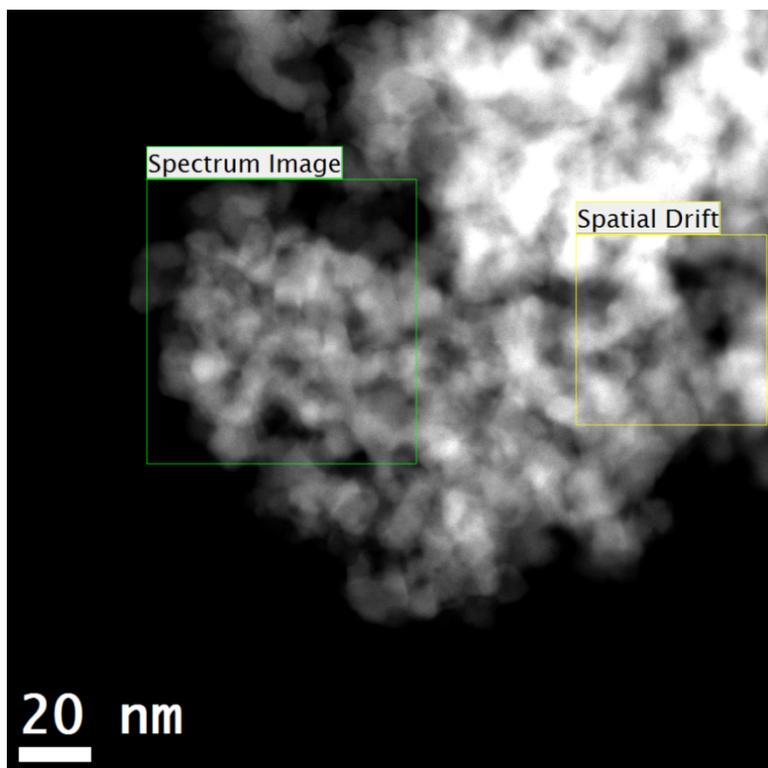
<u>Sample</u>	<u>Fresh(nm)</u>	<u>Aged (nm)</u>	<u>D_{loss} (%)</u>
Cu/CZ	6	27	78
Cu/GMR6	8	11	28



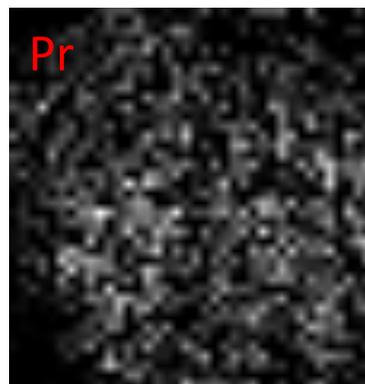
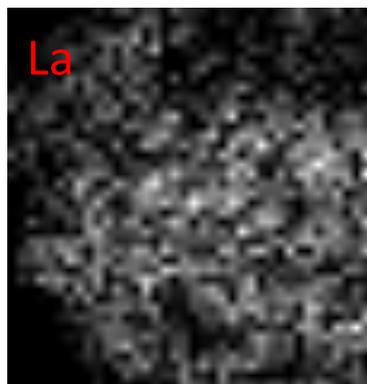
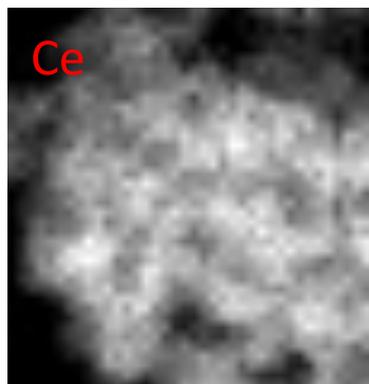
Cu sintering:
Cu species particle size is much greater in aged Cu/CZ than in Cu/GMR6

Chang Kim and coworkers, unpublished.

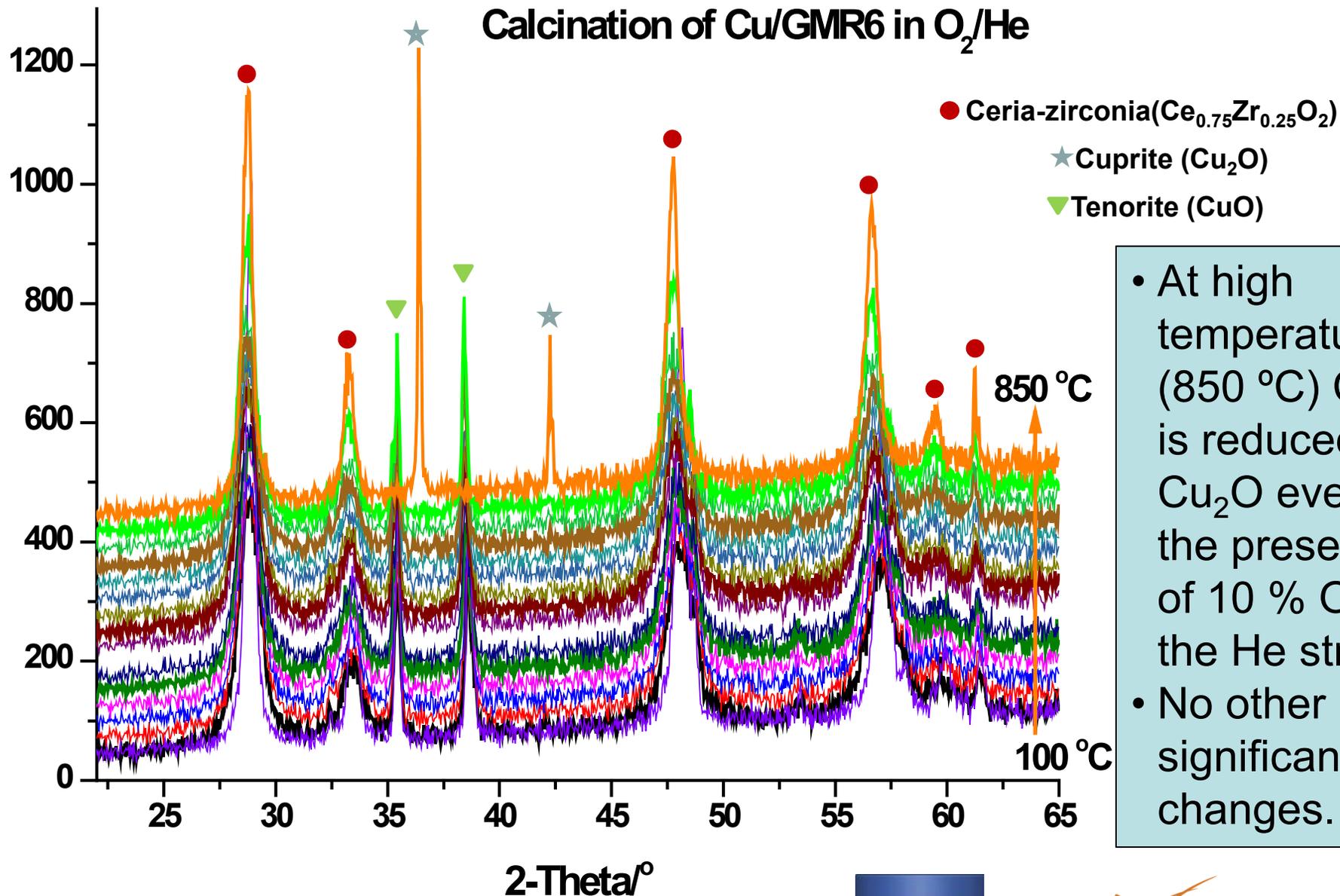




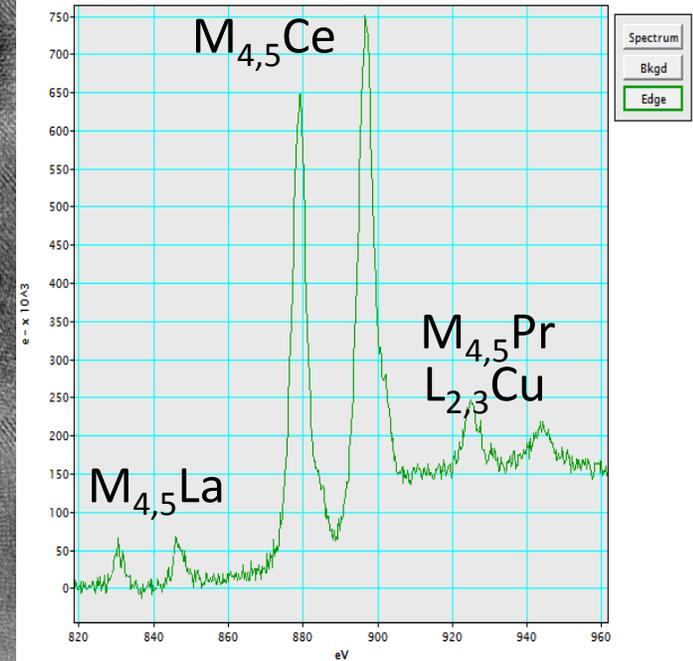
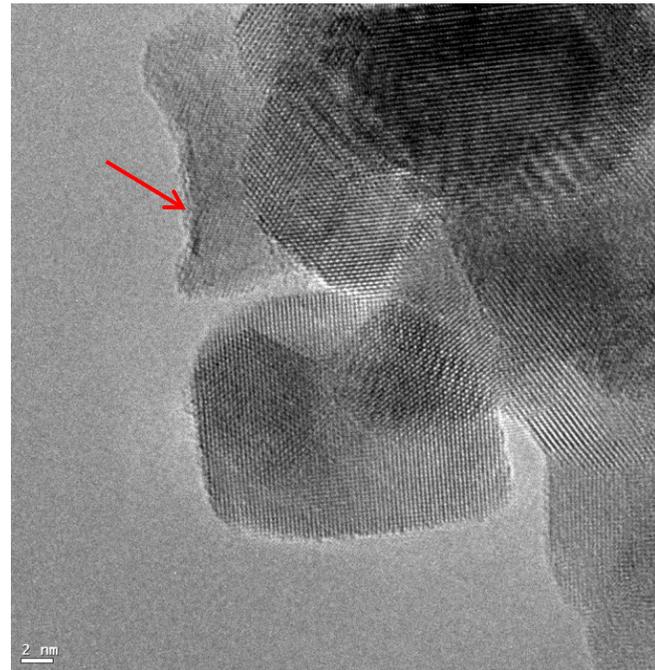
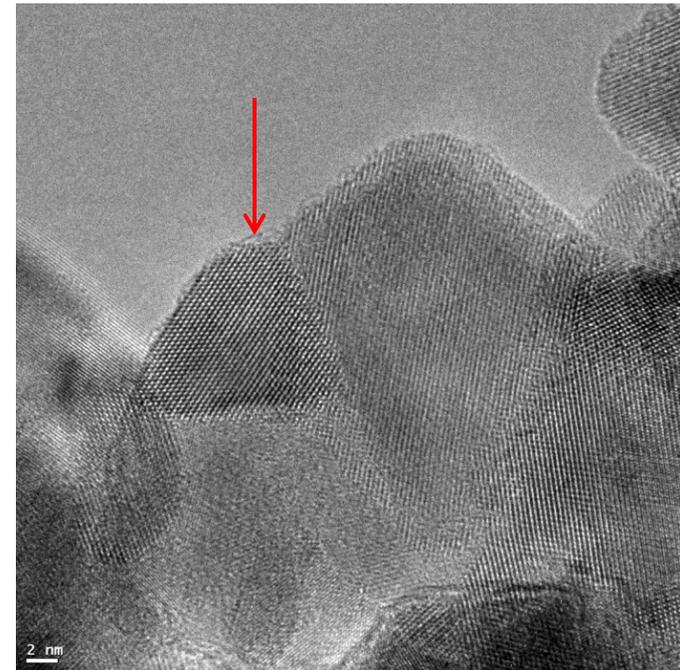
- EELS and EDX analysis clearly shows the presence of evenly distributed Pr and La in the commercial CZ support material
- Pr and La also evident in XPS data (see extra slides)
- These additives may contribute to the enhanced structural stability of this material during hydro-thermal aging



In situ XRD on Cu/GMR6: No significant changes until 850 °C



- At high temperature (850 °C) CuO is reduced to Cu₂O even in the presence of 10 % O₂ in the He stream.
- No other significant changes.



High temperature hydrothermal aging results in the formation of some amorphous phase on the highly crystalline (commercial) CZ support particles.

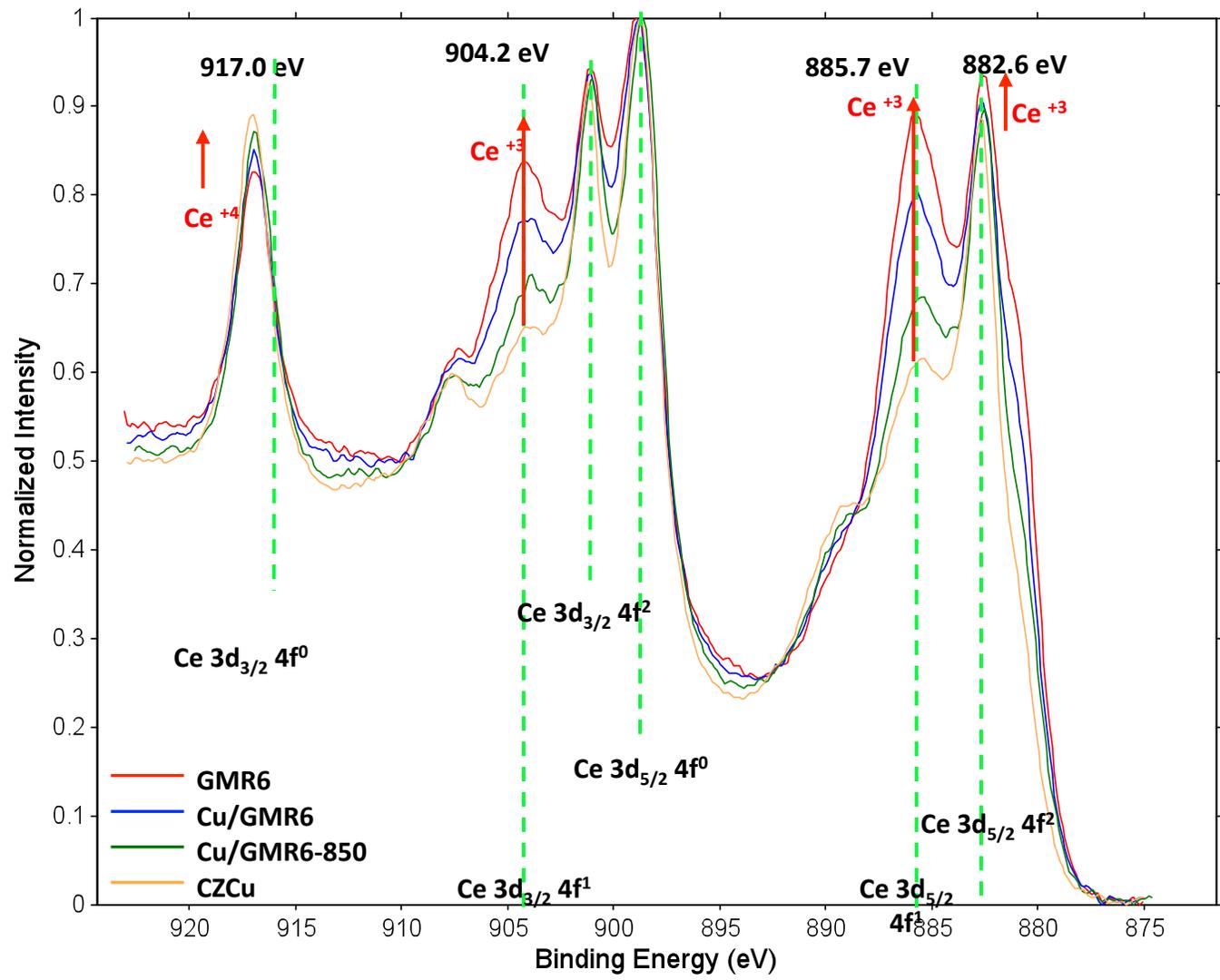
J Szanyi, L Kovarik and
CHF Peden, unpublished.



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Most Active Materials Seem Most Difficult to Reduce by H₂

XPS analysis: Reduction at 500 °C in 10% H₂/He for 1 hr



Extent of Ce reduction:

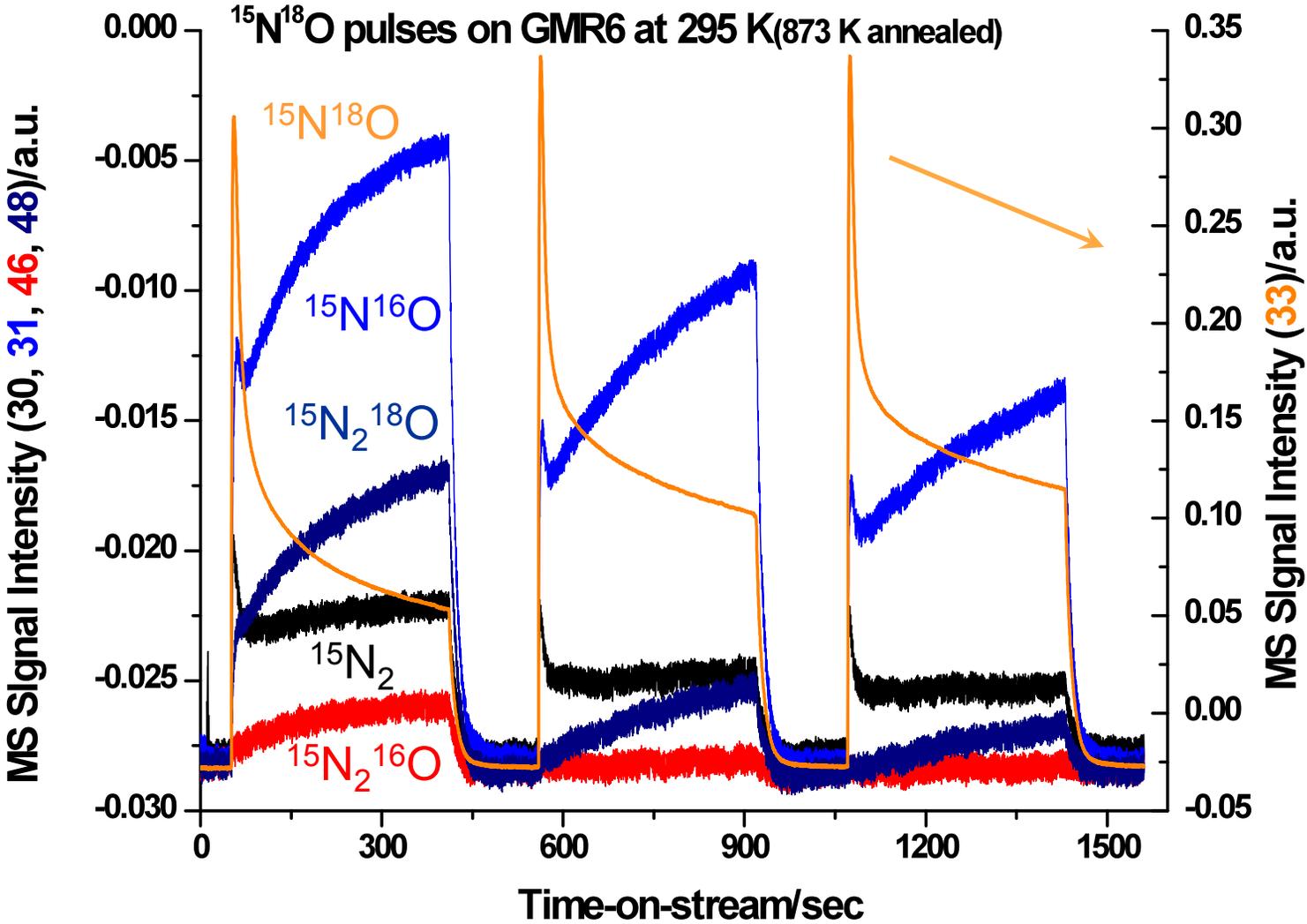
- GMR6 >
- Cu/GMR6 >
- Cu/GMR6 (850 °C aged) >
- CuCZ

Reactivity:

- CuCZ ~
- Cu/GMR6 (850 °C aged) >
- Cu/GMR6

J Szanyi, M Engelhard, and CHF Peden, unpublished.





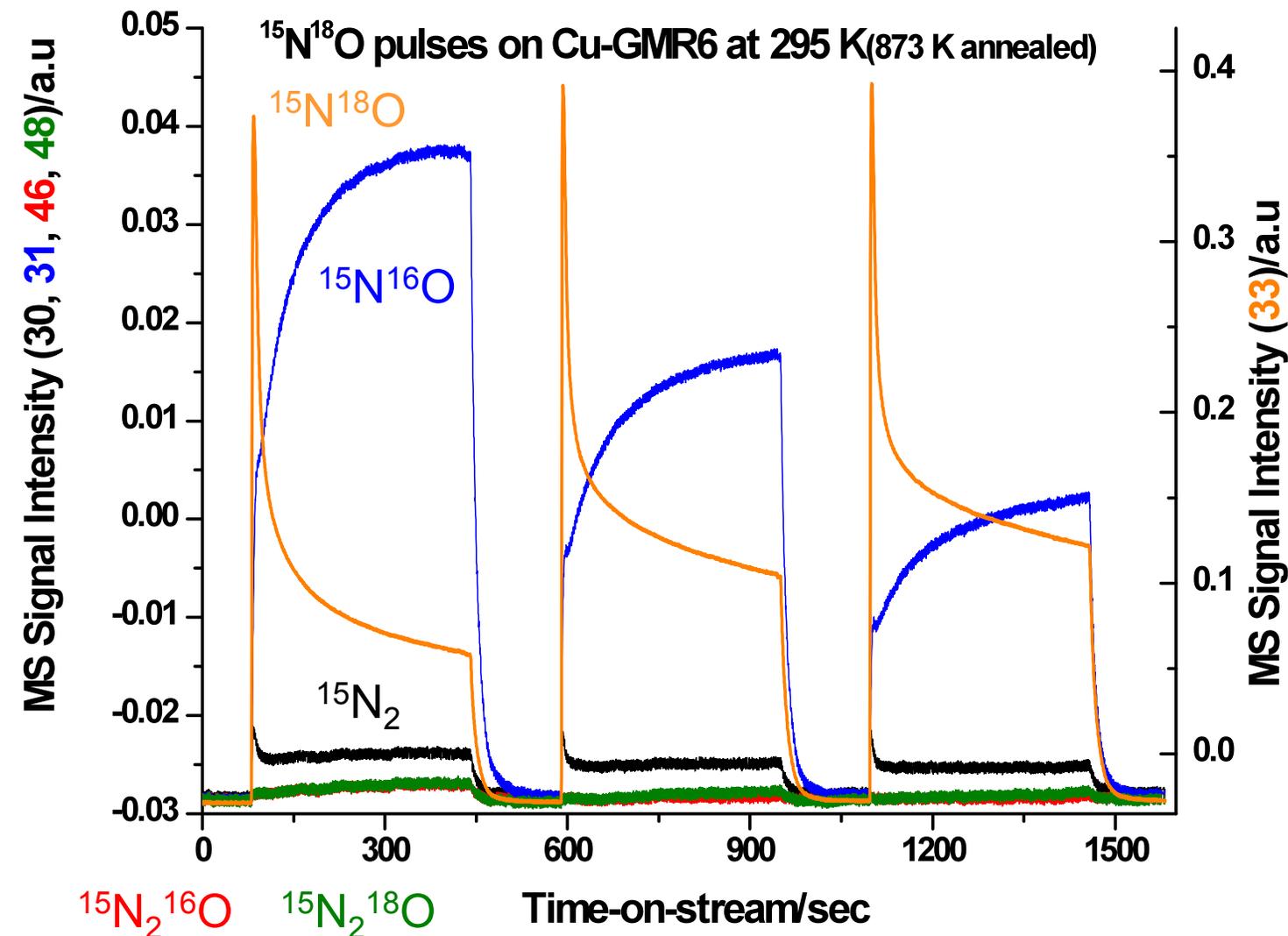
- Extensive oxygen scrambling between $^{15}\text{N}^{18}\text{O}$ and CeZrO_x : highly mobile oxygen in CeZrO_x .
- Curiously, besides oxygen exchange, reduction of $^{15}\text{N}^{18}\text{O}$ also takes place even at 295 K on the 873 K-annealed CeZrO_x support (both N_2 and N_2O are produced, mainly during the first $^{15}\text{N}^{18}\text{O}$ pulse).

J Szanyi, and CHF Peden, unpublished.



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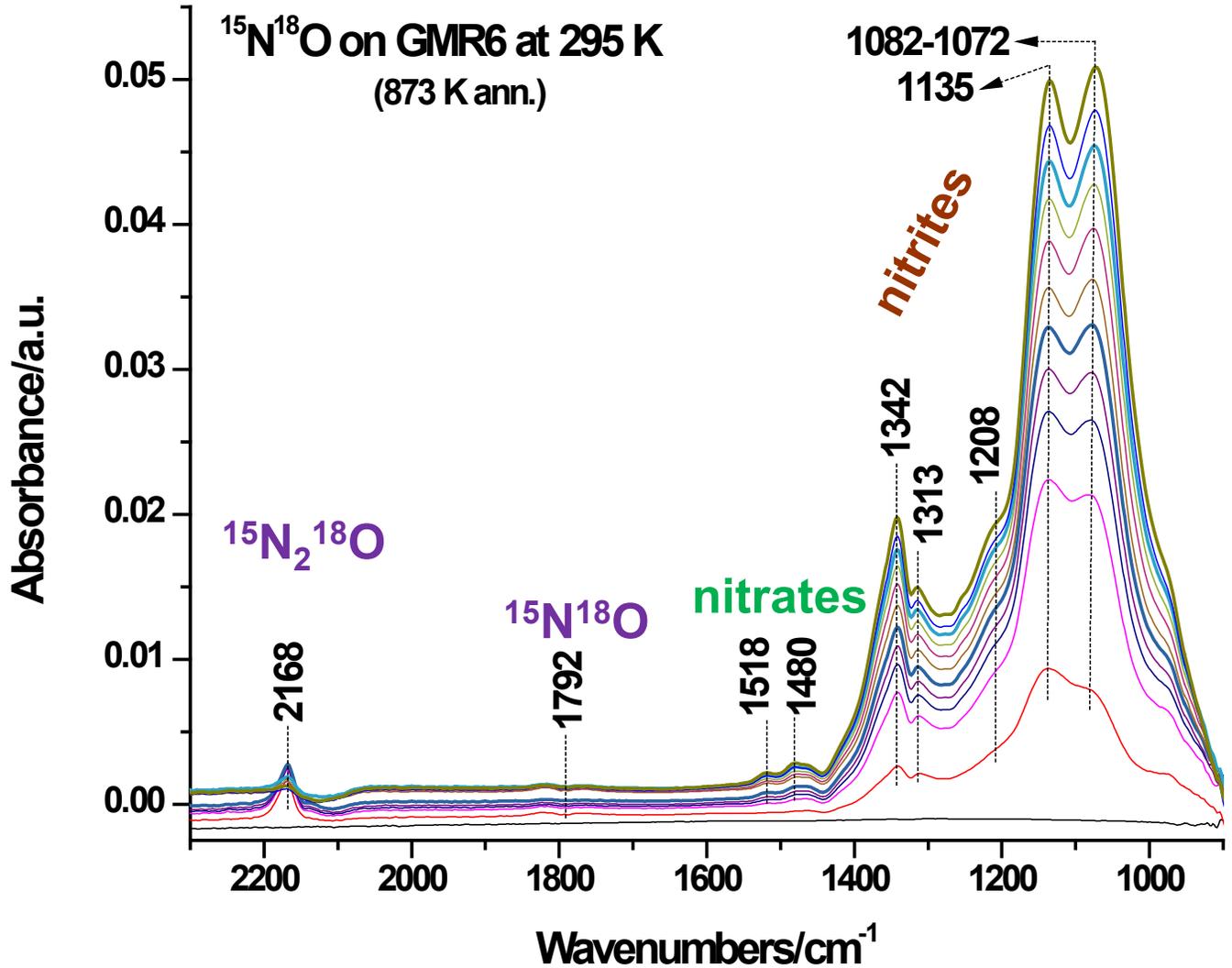
Oxygen mobility on Cu/GMR6 at 295 K – Cu enhancement



- In the presence of Cu, oxygen scrambling is much faster on GMR6 at 295 K.
- The extent of NO reduction seems to be lower than on the support itself.
- Similar results obtained at reaction temperatures (see extra slides)

J Szanyi, and CHF Peden, unpublished.





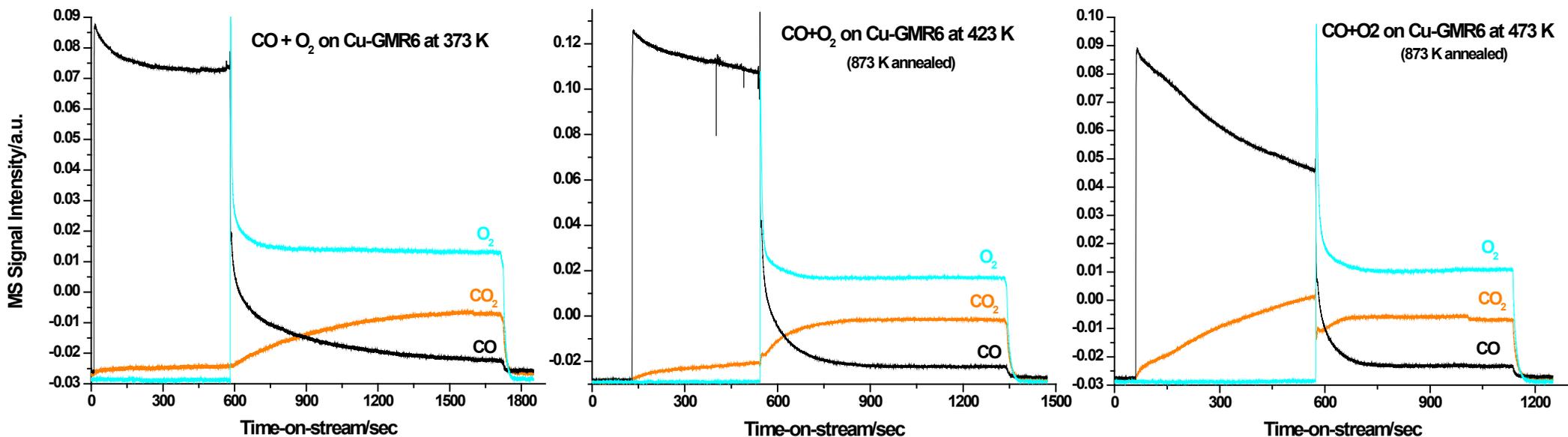
- Both oxygen scrambling between $^{15}\text{N}^{18}\text{O}$ and the support, and NO reduction take place.
- Nitrites form on the support surface.

J Szanyi, and CHF Peden, unpublished.



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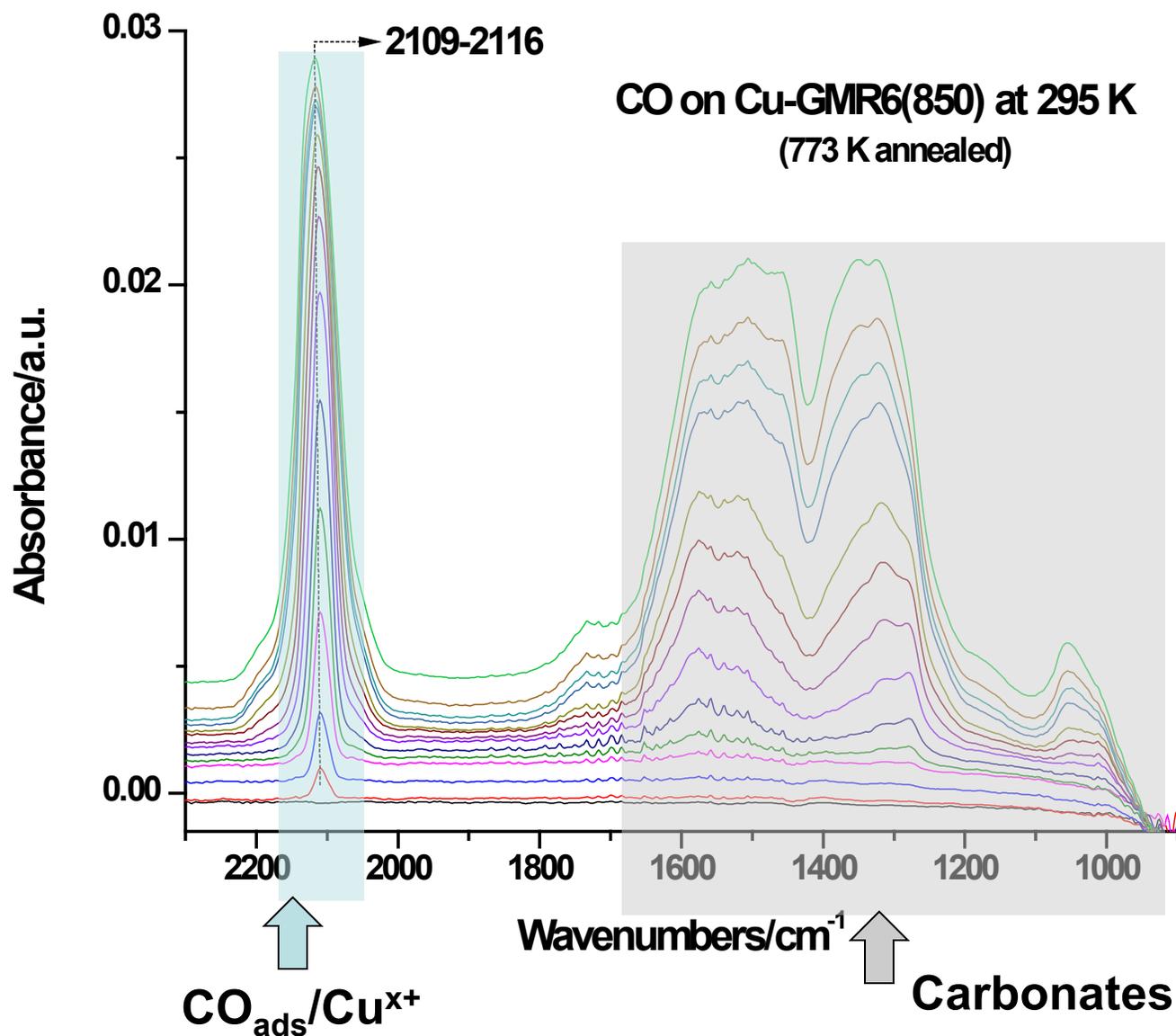
CO+O₂ reaction on Cu/GMR6 in the absence of H₂O and HCs



- With increasing sample temperature, the extent of CO conversion (to CO₂) increases in the absence of O₂ (at 473 K about 1/3 of CO is converted to CO₂ prior to the introduction of O₂)
- In the presence of O₂, CO oxidation is fast even at 373 K.

J Szanyi, and CHF Peden, unpublished.



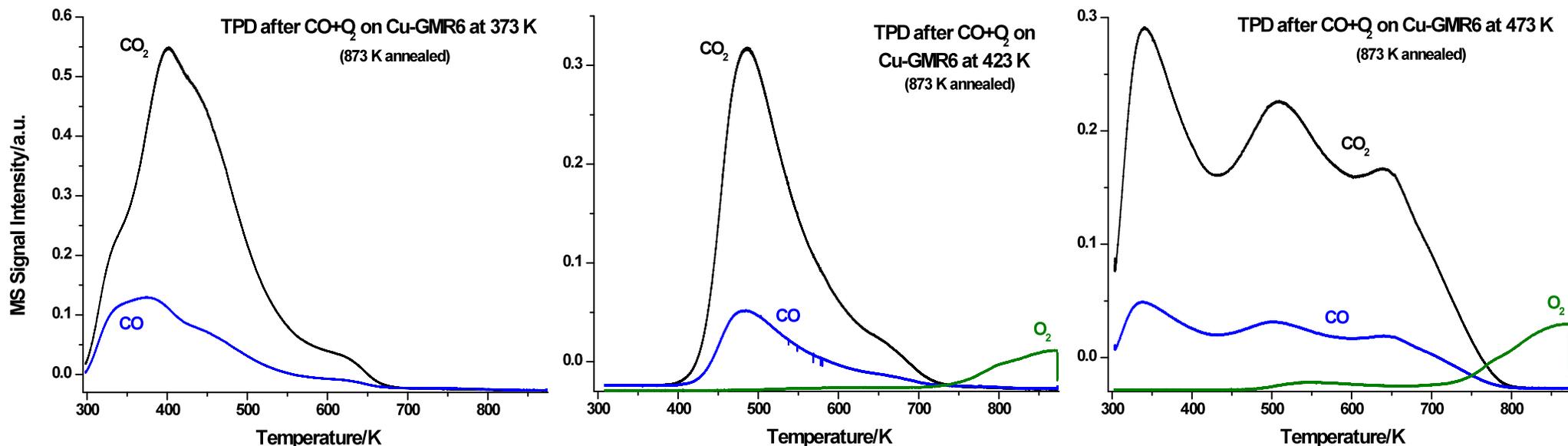


- Extensive carbonate formation at 295 K, even in the absence of O₂
- Again, these results demonstrate the presence of a large pool of mobile oxygen present on the GMR6 support

J Szanyi, and CHF Peden, unpublished.



TPD after CO+O₂ reaction on Cu/GMR6



- During CO oxidation carbonates form on the GMR6 support.
- With increasing reaction temperature the amount of strongly-held carbonates increases.
- After CO+O₂ reactions at temperatures >423K, O₂ desorption is observed at high (>750 K) temperatures.

J Szanyi, and CHF Peden, unpublished.



- 1. Complete initial characterization studies of Cu/ceria-zirconia materials**
 - Include comparison with simple model materials
- 2. Detailed kinetic studies of CO oxidation on fresh and aged Cu/ceria-zirconia catalysts**
 - Kinetics measurements will be especially focused on mechanisms/limitations for low temperature performance (these will include use of the developing CLEERS low-T oxidation protocol)
 - In-situ spectroscopic (FTIR and XAS) measurements
- 3. Synthesis and characterization of new materials**
 - Ceria-supported and mesoporous Cu/ceria materials (recently described in the literature) for baseline mechanistic studies
 - Developing mechanistic understanding and structure/function relationships will guide new materials development efforts
 - Performance and aging studies will be carried out at GM



- Novel low-temperature Cu/ceria-zirconia catalysts synthesized by GM display very promising low temperature CO and hydrocarbon oxidation behavior
 - 1) High temperature aging significantly reduces the CO oxidation activities of CuCZ catalysts.
 - 2) Cu supported on commercial CZ supports (in particular on GMR6) deactivates much less than those prepared on laboratory synthesized CZ supports.
 - 3) Deactivation is due (at least in part) to the large decrease in BET surface area and the large drop in metal (Cu) dispersion during high temperature hydrothermal aging.

- Materials characterization and mechanistic studies have been initiated at PNNL with the following initial results:
 - 1) EDX and XPS analysis revealed that the commercial GMR supports contained both lanthana and praseodymia additives that might act as structural stabilizers for the mixed CZ-oxide support.
 - 2) Isotope exchange experiments with $^{15}\text{N}^{18}\text{O}$ substantiated the very high oxygen mobility in both the GMR6 support and Cu/GMR6 catalyst materials that may contribute to their excellent oxidation abilities (reduction of NO was also observed over these materials even at 295 K).
 - 3) CO molecularly adsorbs on the Cu phase of the Cu/GMR6 catalyst, while carbonates form on the support even at 295 K. The amount of adsorbed CO_2 (carbonate) and its stability on the GMR6 support increase with increasing $\text{CO}+\text{O}_2$ reaction temperature.

